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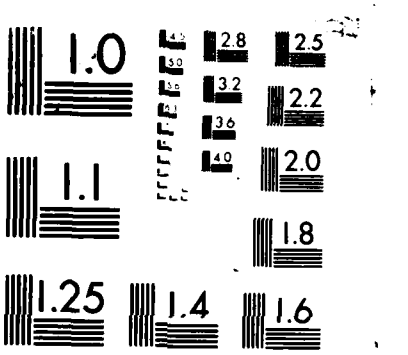

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by

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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF A DIMERIC TRIS(ARSINO)GALLANE CONTAINING A NONPLANAR $(Ga-As)_2$ RING: CRYSTAL STRUCTURE OF $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$*

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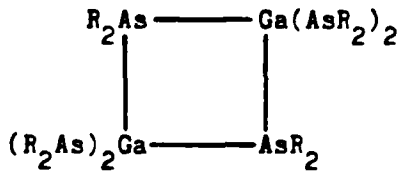
Summary

The dimer $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$, only the second tris(arsino)gallane to be completely characterized, has been prepared from the reaction of $(Me_3SiCH_2)_2AsLi$ with $GaCl_3$; X-ray crystallographic analysis shows it to be the first example of a compound containing a distinctly nonplanar four-membered ring of alternating four-coordinate Ga and As atoms.

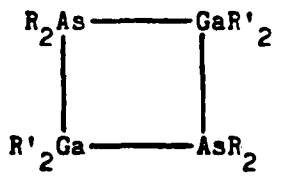
Recently, we applied two new synthetic methods to the preparation of compounds containing a gallium-arsenic bond, viz., dehalosilylation between a silylarsine and a halogallane [1], and coupling using a lithium arsenide and a chlorogallane [2]. Among the compounds prepared by both methods is

*Dedicated to Professor G. E. Coates on the occasion of his 70th birthday.

the first example of a tris(arsino)gallane, monomeric $(Mes_2As)_3Ga$, which X-ray analysis [2] has shown to contain three-coordinate gallium and arsenic. Subsequently, $(Bu^t_2As)_3Ga$ was reported by others, but data for a crystal structure were not obtainable [3]. We now report the structure of a second tris(arsino)gallane, dimeric $[(Me_3SiCH_2)_2As]_3Ga$ (1), prepared by the lithium arsenide method. Interestingly, as noted previously, the reaction of $(Me_3SiCH_2)_2AsSiMe_3$ with $GaCl_3$ did not yield 1 [1]. Compound 1 has a solid state structure containing a distinctly nonplanar four-membered ring of alternating four-coordinate Ga and As atoms. This form contrasts with the planar, centrosymmetric $(Ga-As)_2$ units in $[(Me_3SiCH_2)_2AsGaPh_2]_2$ (2) [4], the first dimeric mono(arsino)gallane for which the structure was reported, and in $(Bu^t_2AsGaMe_2)_2$ (3) [3], and the nearly planar unit in $(Bu^t_2AsGaBu^n_2)_2$ (4) [3], but is similar to, although less puckered than, the novel nonplanar $(Ga-S)_2$ form found in $(Pr^iSGaI_2)_2$ which contains two four-coordinate Ga atoms and two three-coordinate S atoms [5].



1 R = Me_3SiCH_2



2 R = Me_3SiCH_2, R' = Ph [4]

3 R = Bu^t, R' = Me [3]

4 R = Bu^t, R' = Bu^n [3]

A suspension of $(Me_3SiCH_2)_2AsLi$ [6] (2.03 g, 7.9 mmol) in hexane when added [7] to a hexane solution of $GaCl_3$ (0.46 g, 2.6 mmol) at -78 °C gave, after 18 h at room temperature, a brown mixture which, following filtration and solvent removal, redissolved in hexane. Crystallization (-78 °C) and

cold filtration, followed by solvent removal, recrystallization, hexane washings, and drying in vacuo afforded $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ (1) as a pale yellow solid (0.46 g, 22% yield) m.p 71-149 °C (dec.) [8]. Crystals suitable for an X-ray structure determination were grown from a C_6F_6 solution [9].

Crystals of 1 comprise discrete centrosymmetrically-related dimers having the structure illustrated in Figure 1. Several features of this dimer attest to its highly strained nature. Thus, the Ga-As1-Ga'-As1' ring, with a dihedral angle of 13.6° [vs. 36.7(2)° in the $(Ga-S)_2$ ring of $(Pr^iSGaI_2)_2$] between the As1-Ga-As1' and As1-Ga'-As1' planes (mean endocyclic dihedral angle about the ring bonds = 10.2°) is, as shown in Figure 2, distinctly non-planar. Two of the ring bonds, Ga-As1' and Ga'-As1' at 2.540(1) Å, are equal and significantly shorter than the other pair, 2.559(1) and 2.581(1) Å, of which the latter is the longest distance yet reported for such a bond and contrasts with the corresponding longest values of 2.530(1), 2.558(1), 2.557(3), and 2.553(1) Å, respectively, for four-coordinate Ga in dimers 2, 3, and 4, and the unusual $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ (R = Me_3SiCH_2) cluster [10]. All of the ring bonds of 1 are longer than the mean of the essentially equal exocyclic Ga-As bonded distances to three-coordinate As atoms, which, at 2.475 Å, is slightly shorter than the mean Ga-As distance for trigonal planar Ga in monomeric $(Mes_2As)_3Ga$. The mean ring bond angles in 1 (84.81° at Ga, 95.30° at As) are similar to those encountered in dimers 2, 3, and 4 (range: 84.31-85.08° at Ga; 94.92-95.69° at As), but the exocyclic As-Ga-As angles involving the three-coordinate As atoms [122.37(5), 113.68(5)°] differ significantly in response to the different intramolecular interactions involving substituents at each of the Ga centers.

Corresponding exocyclic C-As-C angles show much less variation [103.0(4), 104.7(4)°] indicating the greater resistance of the As centers to bond angle deformation.

Based on the cryoscopic molecular weight, 1 remains intact as a dimer in solution at low temperatures. It appears, however, the dimer is fluxional in solution [the fluxional properties of a dimeric bis(arsino)gallane have been reported] [1] , as indicated by broadening and eventual coalescence of ^{13}C NMR signals as the temperature is increased. Also, compound 1 is thermally unstable in solution at ambient temperatures and above, and slowly decomposes to the diarsine $[(Me_3SiCH_2)_2As]_2$ [1] and unknown products.

Acknowledgement. We thank the Office of Naval Research for financial support.

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6 $(Me_3SiCH_2)_2AsLi$ was produced by the reaction of $(Me_3SiCH_2)_2AsH$ [4] and Bu^nLi in hexane for 2 days at 60 °C, and isolated as an off-white powder.

7 All manipulations were performed under a dry nitrogen atmosphere.

8 Found: C, 35.34; H, 8.29%; mol. wt., 1582 ± 65 (cryoscopic, 0.268 g in 12.22 g cyclohexane). $C_{48}H_{132}As_6Ga_2Si_{12}$ calcd.: C, 35.25; H, 8.13%; mol. wt., 1636. ^1H NMR (300 MHz) (C_6D_6, 21 °C): δ 0.32 (s, exo-Me_3Si), 0.37 (s, endo-Me_3Si), 1.32 and 1.79 (AB pattern, $^2J_{HH}$ 13.8 Hz, exo-CH_2), 1.71 (endo-CH_2); $^{13}C\{^1H\}$ NMR (75.4 MHz) (C_6D_6, 21 °C): δ 0.98 (s, exo-Me_3Si), 2.02 (s, endo-Me_3Si), 6.69 (s, exo-CH_2), 10.59 (s, endo-CH_2).

9 Crystal data: $C_{48}H_{132}As_6Ga_2Si_{12}$ (1), M = 1635.59, triclinic, space group $P\bar{1}$, a 15.050(3), b 25.417(8), c 12.621(4) Å, α 93.73(3), β 110.68(2), γ 77.00(2)°, U 4400.5 Å^3, Z = 2, D_c 1.234 g cm^{-3}, μ(Cu-K_α radiation) = 50.7 cm^{-1}. The crystal structure was solved by direct methods. Full-matrix least-squares refinement of atomic positional and thermal parameters (anisotropic As, C, Ga, Si; fixed methylene H contributions) converged to R = 0.064 [R_w = 0.097; $w = 1/\sigma^2(|F_o|)$] over 8504 absorption-corrected reflections [$I > 3.0\sigma(I)$] recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-K_α radiation, λ = 1.5418 Å; incident-beam graphite monochromator; ω-2θ scans, θ_{max} = 57°). Tables of coordinates, bond lengths and angles, thermal parameters, torsion angles, and observed and calculated structure amplitudes are available from the authors (R.L.W.).

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Legends For Figures

Figure 1. Molecular structure of $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ (1). Selected distances (Å) and angles (°) are: Ga-As1 2.581(1), Ga-As2 2.478(2), Ga-As3 2.476(2), Ga-As1' 2.540(1), Ga'-As1' 2.540(1), Ga'-As2' 2.470(1), Ga'-As3' 2.474(2), Ga'-As1 2.559(1), As1-Ga-As1' 83.58(4), As1-Ga'-As1' 84.04, Ga-As1-Ga' 94.57(4), Ga-As1'-Ga' 96.02(4), As2-Ga-As3 122.37(5), As2'-Ga'-As3' 113.68(5), C111-As1-C121 103.0(4), C111'-As1'-C121' 104.7(4).

Figure 2. The nonplanar $(Ga-As)_2$ ring of compound 1.

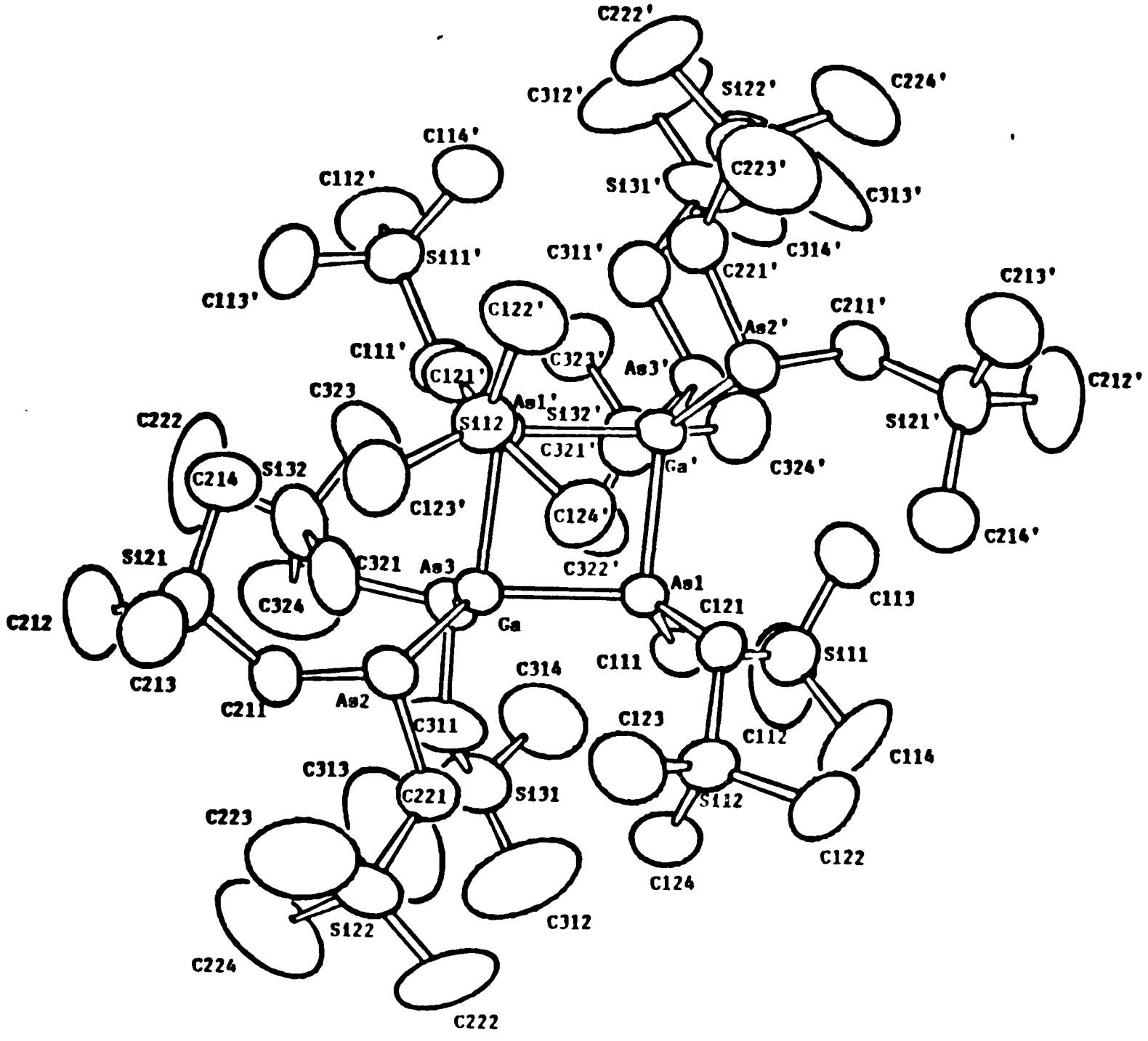
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Figure 1

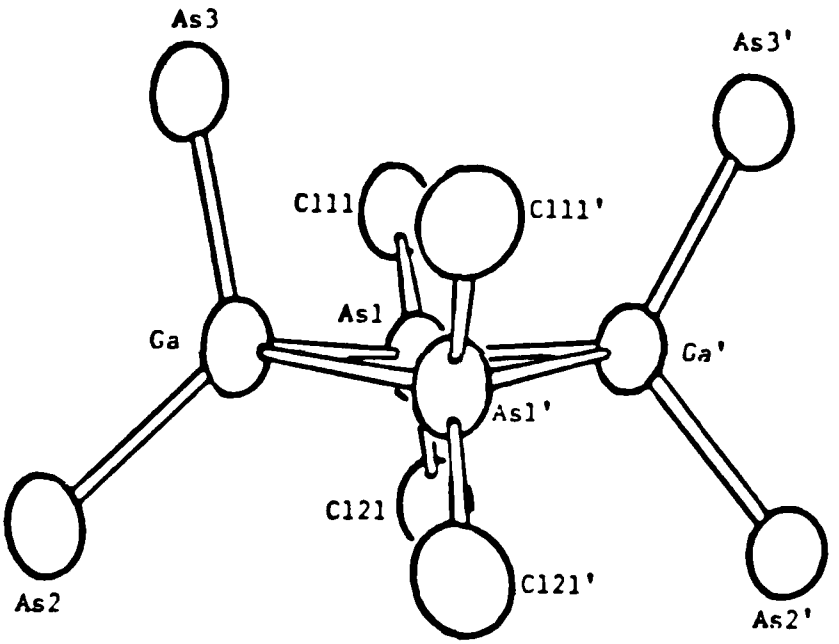

Figure 2

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